

Large Area PECVD Coatings Using Linear Electron Beam Curtains

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ABSTRACT

Large scale web based PECVD processes have been used for some time now to produce clear barrier coatings for food packaging applications. More recently, flexible display and photovoltaic applications have also utilized PECVD processes for producing functional and gas and vapor barrier coatings. Large scale PECVD equipment is usually designed to enhance coating performance, deposition rate and ease of maintenance and cleaning. An alternative approach to microwave and RF magnetron based plasmas is to use a large area plasma generated by a linear electron beam curtain. Such plasmas, which can be further enhanced by magnetic fields have some unique properties that include, plasma generation not requiring electrodes near the substrate area, operation in a broad pressure range, well-defined plasma volume, unique active species concentrations, low internal electric fields, and scalability over multi-meter wide webs. The use of such plasma sources in various configurations applicable to web coating is discussed. Properties of PECVD films such as SiO_x are presented with particular emphasis on vapor barrier properties and potential structural differences resulting from the unique properties of the electron beam generated plasmas.

INTRODUCTION

Sigma Technologies International, in collaboration with the Naval Research Laboratory is developing a materials processing system based on electron beam-generated plasmas for use in range of processing applications. When high-energy (2 keV or greater) electron beams are used as the primary ionization source, the resultant plasmas have unique characteristics when compared to conventional low-pressure plasma sources [1].

Low electron temperature. Conventional plasma discharges rely on externally applied electric fields to raise the plasma electron temperature so that a fraction of those electrons are energetic enough to ionize the gas and sustain the plasma. Because the high-energy electron beam ionizes the gas, electron beam-generated plasmas require no heating of the plasma electrons, which are quickly cooled by elastic and inelastic collisions. The resulting plasma electron temperatures are found to be 1.0 eV or lower [2], depending on background gas. The temperature in molecular gas backgrounds tends to be lower than in noble gases due to the availability of low-energy excitation states. Since the electron temperature

determines the plasma potential [3], ions incident to grounded surfaces will also exhibit low energies [4], typically below 5 eV. If, on the other hand, processes require higher energies, then biasing techniques can be applied [5].

Efficient and controllable ion production. For multi-kilovolt electrons passing through a gas, ionization is the dominant mechanism with the cross-sections being similar for most gases. Thus, little energy is consumed by non-ionizing collisions and species generation can be regulated by adjusting the background gas concentrations [1]. This in contrast to conventional discharges where the dominant inelastic collisions consume most of the delivered energy and ion production favors the species with the lowest ionization potential.

Localized and scalable plasma source. The beam thickness and width are determined by the electron beam source and the length is determined by the beam energy and operating pressure. The plasma production region is limited to the beam volume, which is well defined across an XY plane. For applications that require higher uniformity, the plasma generated by the electron beam curtain can be further collimated by the use of a magnetic field. Hence, the dimensions of the plasma source are tied to the electron beam dimensions, which makes scaling straightforward. Figure 1 shows a schematic of a cold cathode electron beam curtain configured to produce a plasma plane for coating web based substrates.

Outside the beam channel, the plasma density and ion composition are altered by ion-electron, ion-neutral, and ion-ion reactions and so electrodes (or substrates) can be independently positioned to take advantage of the changes in the outwardly diffusing flux of ions and radicals [1]. In conventional discharges, the boundaries of the ionization region are not well defined and increasing the dimensions in a uniform manner can be problematic.

While these attributes can be advantageous in a number of processing applications, they are particularly well-suited for plasma enhanced chemical vapor deposition (PECVD) applications using large area substrates and processes that are not compatible with large ion energies. It is with these ideas in mind that a PECVD process is being developed for the deposition of SiO_x films and coatings using tetraethoxysiloxane (TEOS) as the silicon precursor. The initial

plasma diagnostics and results for films deposited on silicon substrates are discussed.

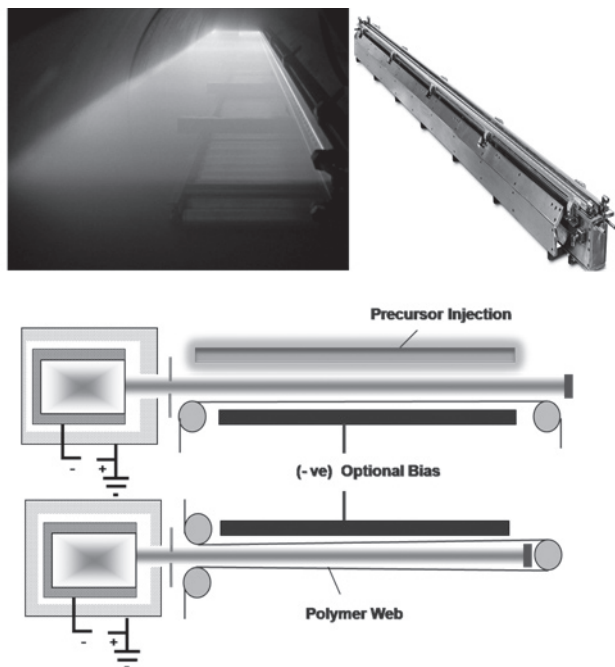


Figure 1: Top: A plasma plane produced by a 3.5m long hollow cathode electron beam curtain (source shown on the right). Bottom: Schematic representation of an electron beam curtain arranged to coat web substrates.

EXPERIMENTAL

Plasma Generation

The general experimental setup has been discussed previously [1] and is shown in the schematic of Figure 2. High-purity argon and oxygen, and the TEOS precursor were introduced by mass flow controllers and an operating pressure of 50 mTorr was achieved by throttling the turbo pump. A beam of energetic electrons was produced by a linear hollow cathode [6] pulsed to 2 kilovolts for 2 ms at a 20% duty factor. The emergent beam passed through a slot in a grounded anode and was then terminated at a second grounded anode located further downstream. The electron beam volume between the two anodes defines the ionization source volume, with the dimensions set by the slot size (1 cm x 25 cm) and the anode-to-anode length (43 cm). Beam spreading from collisions with the neutral background was largely eliminated by a co-axial magnetic field of 150 Gauss that was produced by a set of external magnetic field coils.

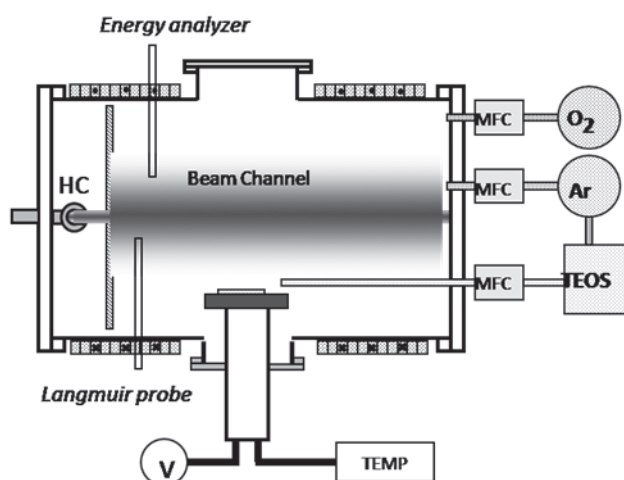


Figure 2: Schematic representation of the experimental set up used to produce SiO_x coatings.

Coating Production

P-type <100> silicon wafers (resistivity 1-20 $\Omega\text{-cm}$) were mounted on a biasable, temperature controlled stage. The substrates were dipped in an 5% HF solution immediately before mounting to the stage and placing in vacuo. The stage was located 2.5 cm from the electron beam axis. In order to increase incident ion energies, an RF generator was used.

At room temperature, TEOS is a liquid with an appreciable vapor pressure ($\sim$ few torr). It was introduced to the system by flowing a fixed amount of argon through a bubbler kept at 18 Torr by a throttle valve between the bubbler and processing chamber. The argon flow through the TEOS bubbler and a separate argon line directly to the chamber were set to total 50 sccm, which allowed a wide range of TEOS gas flow conditions. The TEOS sample was degassed and the gas lines were purged two times before each run. The TEOS gas line to the chamber was heated to prevent condensation. The other reactive process gas was oxygen, also set at a fixed flow of 50 sccm, bringing the total gas flow to 100 sccm for the process.

Inside the chamber, the TEOS was introduced approximately 1 cm in front of the sample stage. The oxygen and independent argon gas lines were introduced approximately 40 cm away at the wall of the chamber, with no special relation to the substrate or e-beam. The sample stage was electrically grounded for this work and could be heated or cooled. The stage temperature was reached rapidly (20-30 min) and allowed to equilibrate

for 10 min. As an additional cleaning step before any TEOS was introduced, a 50 mTorr argon/oxygen plasma (50 sccm each) was run for 20 minutes. TEOS was then introduced by opening the bubbler isolation valve and adjusting the two argon flows to maintain a 100 sccm total. The growth continued at 50 mtorr for 3 to 3.5 hours and was monitored with an in situ HeNe laser reflectometer. After deposition, the TEOS reservoir was again isolated from the system and an argon/oxygen post-treatment plasma was again run for 20 minutes. For all plasma steps, the e-beam was modulated in time, having a fixed 2 ms duration and 20% duty factor.

After the plasma post-treatment, the stage heating or cooling was turned off and the sample was allowed to come to room temperature. The sample was removed from vacuum and the film thickness was measured using a white-light spectrophotometer. The composition of the SiO_x films were analyzed by FTIR (Nicolet Magna 750; MCT detector and 4 cm^{-1} resolution) and by wet etching in a "P-etch" solution [7] of 15 HF:10 HNO_3 : 300 H_2O (by volume).

RESULTS AND DISCUSSION

The focus of our work to date has been to identify the key operating parameters that influence film growth rate and quality. The growth rate of SiO_x was studied as a function of voltage bias on the substrate. All films were etched using the P-etch solution and the resulting etch rates varied between 20 and 200 nm/min, suggesting the films were porous. The results as shown in Figure 3, demonstrate that both the growth rate and resistance to etching increases with substrate bias, suggesting that the higher bias increases the ion flux and energy at the substrate, which in turn increases the deposition rate and density of the SiO_x films.

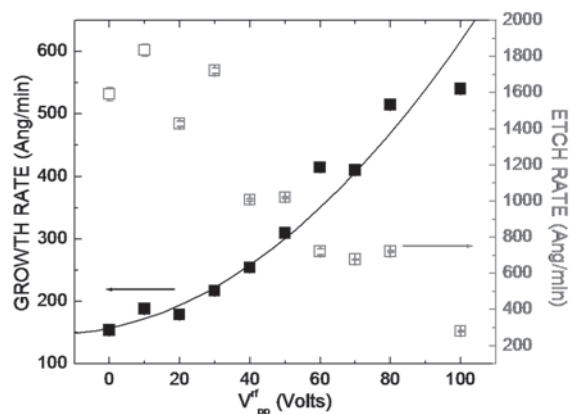


Figure 3 Sample bias increases both the growth rate and chemical resistance (or density) of the SiO_x films.

Figure 4 shows FTIR results for films produced at different substrate temperatures. The measurements reveal that coatings produced at lower temperatures have a significant level of hydrogen integrated in the oxide structure. The Si-O-Si band

signatures are clearly present at 1100 cm^{-1} (stretch), 810 cm^{-1} (bend), and 450 cm^{-1} (rocking) for all process temperatures. What is also evident from the data is the evolution of Si-OH (3500 cm^{-1} and 930 cm^{-1}) and H-OH (3300 cm^{-1} and 1700 cm^{-1}) at lower stage temperatures. This suggests the films grown over the range of temperatures will vary in chemical structure. It should also be noted that none of the films appear to contain any of the aliphatic chain groups ($-\text{CH}_2-\text{CH}_3$) of the precursor (2900 cm^{-1}).

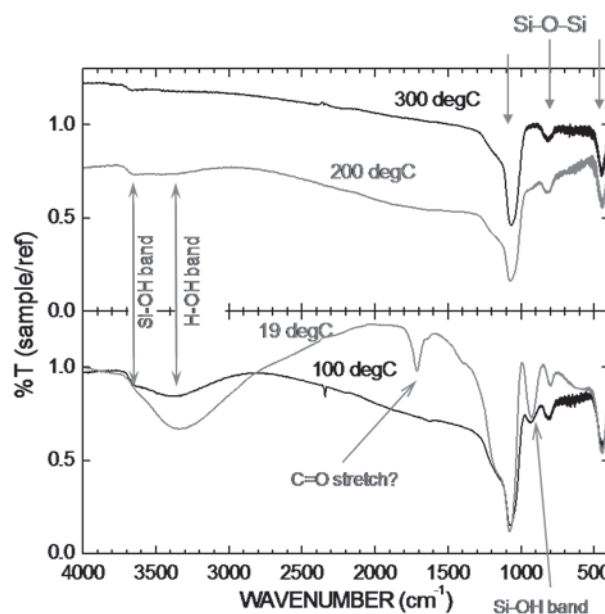


Figure 4 FTIR Spectra of SiO_x films produced at different temperatures. The results show that coatings produced at lower temperatures incorporate H bonds in the coating structure.

SUMMARY

Results from preliminary investigations of PECVD of SiO_x films and coatings using an electron beam-produced plasma source were presented. The experimental results show that the deposition rate of SiO_x films and resistance to chemical etching increase with substrate bias. This suggests that enhanced ion bombardment improves the coating density and adds to the deposition rate. The SiO_x film chemistry was found to depend on substrate temperature. At temperatures below 150°C the coatings contained a significant amount of H in the SiO_x lattice structure, while higher temperature coatings were a pure oxide. The ultimate goal of this work is to develop a process compatible with the deposition of SiO_2 films on large area, flexible substrates. Future work in this area will focus on lower temperature, higher deposition rate coatings on polymer film substrates.

ACKNOWLEDGEMENTS

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